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## Selective Homogeneous Catalytic Oxidation of Olefins using Oxygen/Hydrogen Mixtures: Oxygen Atom Transfer from an Iridium Hydroperoxide

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An iridium(III) hydride complex in solution catalyses the  $O_2$ -co-oxidation of cyclo-octene and  $H_2$  to cyclo-octanone and water, respectively, *via* a hydroperoxide intermediate.

The selective  $O_2$ -oxidation of olefins to ketones by a single oxygen atom transfer process catalysed by rhodium complexes has been well documented.<sup>1,2</sup> In some systems the second oxygen atom of the  $O_2$  molecule is reduced by a twoequivalent reducing agent, and analogies can then be drawn to the general reaction (1) of monoxygenases such as cytochrome P450.<sup>2-4</sup> The preferred electron donor in the enzyme system is the hydride of NADH, and this coupled with the reported rhodium(III)-catalysed co-oxidation of dimethyl

$$X + O_2 + 2e \xrightarrow{2H^+} XO + H_2O; (X = substrate)$$
 (1)

$$Me_2SO + O_2 + H_2 (or H^- + H^+) \rightarrow Me_2SO_2 + H_2O$$
 (2)

sulphoxide and hydrogen according to equation (2), in which the oxygen-carrier appeared to be a rhodium(III) hydride,<sup>5</sup> led us to test the use of  $H_2$  as co-reductant for monoxygenasetype activity with olefinic substrates. This communication reports the successful catalytic oxidation of cyclo-octene to cyclo-octanone according to equation (3) using dimethylacetamide (DMA) solutions of the 1,5-cyclo-octadiene dimer

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$$C_8H_{14} + O_2 + H_2 \rightarrow C_8H_{14}O + H_2O$$
 (3)

$$\operatorname{IrCl}(C_8H_{12})(\mathrm{DMA}) + \operatorname{HCl} \rightleftharpoons \operatorname{IrHCl}_2(C_8H_{12})(\mathrm{DMA})$$
 (4)

 $[IrHCl_2(C_8H_{12})]_2$ ,<sup>6</sup> or mixtures of the  $[IrCl(C_8H_{12})]_2$  dimer<sup>7</sup> with HCl that form the solvated monomeric hydride (1) according to equation (4), K = ca. 10<sup>4</sup> l mol<sup>-1</sup> at 20 °C; an iridium(III) hydroperoxide (IrOOH) is a likely intermediate.

Typically, DMA solutions of (1) (ca. 0.03 м) in the presence of at least a ten-fold excess of cyclo-octene and a five-fold excess of HCl (conveniently added as the DMA adduct) absorb gas from hydrogen/oxygen mixtures at a total pressure of 1 atm and temperatures of 5-30 °C to generate catalytically cyclo-octanone and water as products.‡ The reactions are slow; thus at 5 °C with 350 Torr of each gas, the turnover for cyclo-octanone per iridium is about two per day based on week-long experiments. The amount of water formed is greater than expected from the stoicheiometry of equation (3) because of a competing catalytic hydrogenolysis of the oxygen;8 at the early stages of reaction the H<sub>2</sub>O: cyclooctanone product ratio was about 40, but this decreased to a steady value of about 10 after one day. Importantly, no oxygenation of cyclo-octene occurs at all in the absence of H<sub>2</sub>, and the absence of any inhibitory effect of radical inhibitors rules out a free-radical autoxidation reaction. Much higher rates are achieved at 30 °C but the oxygen hydrogenolysis becomes even more dominant.

Evidence for a plausible mechanism comes from the reactivity of (1) towards oxygen. At 1 atm pressure and 5 °C, (1) in DMA absorbs 1.0 mol of  $O_2$  per iridium, but no free oxygenated organic compound is detected. A suspension of the hydride dimer in  $CH_2Cl_2$  similarly absorbs  $O_2$  to a 1:1 ratio to give a deep-red solution that is conveniently monitored by i.r. The v(Ir-H) band (2260 cm<sup>-1</sup> in the solid) is replaced by a strong band at 3495 cm<sup>-1</sup>, considered to be the v(O-H) of hydroperoxide;9 this band decreases in intensity and disappears with time as new bands intensify at 3680 and  $3605 \text{ cm}^{-1}$  [attributed to v(O-H) of hydroxide], and at 1692 and 1607 cm<sup>-1</sup> [attributed to the v(C-O) of free<sup>10</sup> and coordinated 4-cyclo-octen-1-one, respectively]. Addition of triphenylphosphine replaces the co-ordinated ketone which is accompanied by a corresponding decrease of the 1607  $cm^{-1}$  band. The data are consistent with reaction (5), written for a monomer, showing oxygen-atom transfer to the diene from an iridium hydroperoxide intermediate. Such metalcatalysed atom transfer to olefins has been postulated but not previously demonstrated,<sup>1,2,9</sup> although transfer from alkylperoxides is well documented; metallocyclic intermediates are likely to be involved.<sup>1,11</sup> Insertion of O<sub>2</sub> into metal hydride

$$IrHCl_{2}(C_{8}H_{12}) \xrightarrow{O_{2}} Ir(OOH)Cl_{2}(C_{8}H_{12}) \xrightarrow{} \\ `Ir(OH)Cl_{2}' + C_{8}H_{12}O \qquad (5)$$

bonds is known for some rhodium(III) systems.<sup>12</sup> Reaction of the iridium(I) dimer  $[IrCl(C_8H_{12})]_2$  with  $O_2$  is reported to give a hydroxyiridium species with no oxidation of the diene<sup>13</sup> (and we have failed to detect oxygenated diene), which gives indirect evidence for a role of the hydride ligand in reaction (5). The cyclo-octenone was detected also in the catalytic cyclo-octene oxygenation described above; presumably removal of the diene by reaction (5) provides vacant or 407

solvated sites for subsequent co-ordination of the monoene. Addition of an excess of cyclo-octadiene to the  $[IrHCl_2-(C_8H_{12})]_2$  system under  $H_2/O_2$  did not result in catalytic oxidation to the cyclo-octenone. The catalysis requires regeneration of the hydride from the 'Ir(OH)Cl<sub>2</sub>' species, and this could involve a net heterolytic splitting of  $H_2$  by such an iridium(III) species, either before or after a protonation step, equation (6). Reaction (5) is more rapid than the catalysis, which indicates that the slow step in the catalysis

$$Ir(OH)Cl_{2} + H_{2} \rightarrow IrHCl_{2} + H_{2}O$$

$$H^{+} \downarrow \qquad -H^{+}, H_{2} \uparrow \qquad (6)$$

involves hydride regeneration. The data imply that, compared to a monoene, the more strongly co-ordinating diene inhibits reactions such as (6).

Use of  $H_2/O_2$  mixtures richer in  $H_2$  for the cyclo-octene oxidation also produces some cyclo-octane via a catalytic hydrogenation process; such hydrogenation involves intermediate alkyls and reaction of these with O<sub>2</sub> to give alkylperoxides (e.g.,  $Ir-O_2R$ ) also could provide a pathway for the oxygenation. However, the experimental evidence for reaction (5) leads us to a working hypothesis invoking reactions (5) and (6) for the net catalysis. Although the reaction discovered is very inefficient, it does prove the potential of using  $H_2$  as the co-reductant in monoxygenase-type catalysis. Although the use of  $H_2/O_2$  mixtures sounds alarming, we have experienced no difficulties under the mild conditions used. Borohydride has been used recently as co-reductant in catalytic oxygenation of olefins using a manganese(III) porphyrin; non free-radical pathways involving a hydroperoxide were again invoked (Mn<sup>III</sup>-OOH  $\leftrightarrow$  Mn<sup>IV</sup>=O).<sup>3</sup>§

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§ Added in proof: A report (I. Tabushi and A. Yazaki, J. Am. Chem. Soc., 1981, 103, 7371) that appeared after submission of this communication describes the use of  $H_2$  with colloidal platinum as the electron donor with the same manganese porphyrin/O<sub>2</sub> system for epoxidation of olefins.

<sup>&</sup>lt;sup>‡</sup> Products were identified by g.c. and m.s.; OV-101/chromasorb and Porapak Q were the g.c. column materials for the organic products and water, respectively, using 2-bromomesitylene and methanol as internal standards.